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Potential Cd emissions from end-of-life CdTe PV

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Abstract
Purpose Cadmium telluride photovoltaics (CdTe PV) have grown considerably in the last few years and are now a mainstream energy technology. Concern has been voiced regarding the potential impact caused by the dispersal of the Cd contained in the modules after they are decommissioned. This study presents a new comprehensive analysis of the end-of-life of CdTe PV and reports on the associated Cd emissions to air and water.
Methods Three end-of-life scenarios were considered for CdTe PV. In the first one, 100% of the modules are collected and sent to recycling; in the other two, 85% of the modules are recycled, and the rest are assumed to be either treated as normal municipal solid waste or pre-selected and sent to landfills. All input and output data for module decommissioning and recycling were based on the information directly provided by the world-leading CdTe PV manufacturer (First Solar). The inventory modelling was performed with the GaBi life cycle analysis software package in conjunction with the Ecoinvent v.2 database.
Results and discussion In all scenarios, end-of-life Cd emissions from CdTe PV were found to be relatively low, for instance when compared to those from NiCd batteries, when expressed per kilogram of Cd content.
Conclusions The on-going growth of CdTe PV is unlikely to produce a worrisome increase in the overall Cd emissions to the environment; principally thanks to the expected stringent control of the related Cd-containing waste flows.

Keywords Cadmium · CdTe PV · Emissions · End-of-life · Photovoltaics · Recycling

1 Introduction

Photovoltaics (PV) stand among the most promising technologies in the whole renewable energy sector, with almost 40 GWp of installed power worldwide in 2010 (Jaeger-Waldau 2011; Fig. 3, p. 15), and estimates indicate that their growth is likely to be sustained in the future, leading to between 80 and >200 GWp of installed capacity as early as 2020, depending on the adopted scenario (Jaeger-Waldau 2011, p. 112). Within the PV sector as a whole, cadmium telluride (CdTe) PV has been gaining market share due to its comparatively lower production cost and lower energy and material demands during production, and it already represents over 5% of the global PV market (Hering 2011) vs. only 1.6% in 2006 (EPIA 2006). In parallel to experiencing commercial success, CdTe PV has been widely shown to be characterised by sound environmental performance in terms of energy pay-back time, global warming potential and acidification potential (Fthenakis and Alsema 2006; Fthenakis and Kim 2007; Raugei et al. 2007; Fthenakis et al. 2008, 2009; Raugei and Frankl 2009). The Cd emissions associated to PV module production have also been the object of scientific scrutiny, and when expressed per kilowatt hour of electricity delivered, they turned out to be no higher than those from competitive PV technologies and at least one order-of-magnitude lower than those for conventional electricity

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from fossil fuels (Fthenakis 2004; Fthenakis et al. 2008). Moreover, since Cd is an unavoidable by-product of Zn mining, the consequences of a large-scale deployment of CdTe PV in terms of sequestration of potentially harmful left-over stockpiles of raw Cd are to be considered (Raugei 2010). In fact, information on the environmental fate of Cd-rich residues from Zn-mining activities is scarce. A large surplus of Cd is theoretically recoverable from Zn ores, but since there is currently no viable market for it, a large fraction of it ends up being not even properly accounted for in official reports. While such large quantities of Cd are not directly classifiable as actual emissions flows, the sheer lack of information on their management is enough reason for concern. New technologies, such as CdTe PV, which provide safe and non-dissipative uses for it, may thus even end up having an overall negative, rather than positive, Cd emission budget (Raugei and Fthenakis 2010). Since the very beginning of its introduction to the market, though, CdTe PV has been the object of understandable concern specifically regarding the potential impact on the environment and human health caused by the dispersal of the Cd contained in the modules after they are decommissioned.

In the European Union, the use of Cd in products has long been strictly regulated by Directive 91/338/EEC; the latter does not directly apply to CdTe PV, though, because Cd is only present in the PV modules in non-metallic form, which is generally considered to pose a less serious health threat. In particular, acute oral toxicity tests performed on rats have determined the median lethal dose (LD50) for CdTe to be greater than 2,000 mg/kg, which marks it as not only less toxic than metallic cadmium (Zayed and Philippe 2009), but also considerably less so than cadmium oxide, for which the oral LD50 in rats is 72 mg/kg (Merck 2006). Studies on the toxicity of tellurium are scarce; the element itself appears to be only mildly toxic and not carcinogenic (Harrison et al. 1998); Yarema and Curry reported that two subjects intoxicated through accidental ingestion of solutions containing substantial concentrations of tellurium dioxide recovered without serious sequelae (Yarema and Curry 2005).

Directive 2002/95/EC on the Restriction of Hazardous Substances then went on to ban the use of cadmium altogether in a wide range of electronic and electric equipment covered by companion Directive 2002/96/EC on Waste of Electrical and Electronic Equipment (WEEE). So far, PV has not been included under the scope of either of these directives, but amendments are possible in future revisions of the directives' annexes.

In any case, regardless of the eventual inclusion of PV in the WEEE directive, recycling is clearly the most advisable decommissioning strategy for CdTe PV modules. In this way, not only can potential Cd pollution be limited by avoiding the risk of Cd being emitted into the environment, but a considerable advantage is also obtained from the points of view of the energy and raw material demand, the latter being key to the technology's long-term sustainability (Fthenakis 2009). To ensure that the modules are indeed recycled, a take-back policy has been implemented by the current leading manufacturer, First (2011), whereby sufficient funds are set aside to meet the estimated costs of collecting and recycling modules at the end of their useful life. CdTe PV recycling plants are already operational at all of First Solar's manufacturing sites, in the USA, Malaysia and Germany. New CdTe PV manufacturers are likely to be induced in following this example, and this is in fact already happening in two known instances (Abound Solar 2011; Calyxo 2011).

PVCYCLE, the European voluntary PV recycling initiative representing more than 85% of the European PV market, launched the first large-scale dismantling of end-of-life solar panels in France in May 2009 (Larsen 2009). PVCYCLE members also signed a declaration in 2009, committing to benchmarks of 65% collection and 85% recycling targets (Clyncke 2010); on the basis of voluntary agreements, the minimum collection rate is then expected to quickly rise to 80% by 2011 and 85% by 2012 (PVCYCLE 2007).

The hitherto lack of a detailed analysis of the Cd flows associated to the end-of-life treatment of the CdTe PV modules was the motivation for the work being presented here, which represents an important original contribution to the field of cadmium industrial metabolism. A new comprehensive analysis of the end-of-life of a modern CdTe PV system has been performed, based on first-hand data from industrial-recycling processes. Results in terms of Cd emissions to air and water are presented and discussed.

2 Methods

Three scenarios were considered for the end-of-life of CdTe PV, respectively called 'best case', 'reference' and 'worst case'. The 'best case' scenario corresponds to the limit case of an ideal, perfectly functional take-back and recycling scheme being implemented by all CdTe PV producers, whereby 100% of the decommissioned CdTe PV modules are collected and sent to recycling. The second and third scenarios both assume the minimum collection target set by PVCYCLE for 2012, whereby 85% of the PV modules are effectively collected and sent to recycling, and 15% escape collection and end up in undifferentiated municipal solid waste (MSW). These

two scenarios are then differentiated by assuming a different fate for the non-recycled 15%: in the 'reference' scenario, the PV modules are separated out in the MSW selection and re-treatment plants and they are sent to landfills; in the 'worst case' scenario, instead, they just follow the common fate of the unsorted MSW and are thus partly landfilled and partly incinerated.

A life cycle inventory of the decommissioning and final treatment (disposal and/or recycling) of a large-scale ground-mounted CdTe PV installation was performed, according to the current ISO standards (ISO 2006a, b). This included all the required direct inputs and background processes for PV module recycling, as well as the associated direct and indirect emissions to air and water. All of the inventory modelling was performed making use of the GaBi Professional life cycle analysis software package (PE International 2006), and the choice was made to source background processes from Ecoinvent v. 2.01 (Swiss Centre for Life Cycle Inventories 2007).

The input and output data for module decommissioning and recycling were based on the information directly provided by the manufacturer (First Solar) for their German recycling plant, and, consistently, the German electricity mix (medium voltage) was employed in the analysis. The PV module recycling process is schematically illustrated in Fig. 1.

First Solar's process analysed here is the only recycling method for CdTe PV modules that has been tested on a full production scale so far (Held 2009) and is a variant of the one originally proposed by Bohland et al. (1998a, b), employing a dilute solution of sulphuric acid and hydrogen peroxide as leachant. The cadmium and tellurium are then precipitated by adding NaOH and filtered from the solution together, in the form of a 'filter cake'; 94% and 91% recovery rates, respectively, for Cd and Te were reported to have been regularly achieved. The non-recovered metals (i.e. 6% of Cd and 9% of Te) are sent to a wastewater treatment facility, which is reported (First Solar 2009) to reduce the Cd concentration in the water outflow to the environment to 0.07 ppm, i.e. well below the current 0.2 ppm action limit in the European Union (Directive 83/513/EEC). The Cd emissions to freshwater from the module recycling process were therefore calculated as:

$$0.07\text{mg(Cd emitted)/kg(water output)} \cdot 4.9\text{kg(water output)/m}^2\text{(PV module)} = 0.34\text{mg(Cd emitted)/m}^2\text{(PV module)}$$

$$\Rightarrow \text{Cd emissions to water from recycling process : } \left[0.34\text{mg(Cd emitted)/m}^2\text{(PV module)}\right] / \left[9.7\text{g(Cd)/m}^2\text{(PV module)}\right] = 0.035g\text{(Cd)}$$

emitted *per kg of Cd content in PV module scrap.*

After this step, an open-loop recycling model was adopted (Guinée 2001), whereby the emissions associated to the re-processing of the filter cake into high-purity Cd and Te (performed by industrial partner 5N-Plus in Germany and Canada) are to be wholly attributed to the downstream product systems which make use of the purified metals. Consistently, no environmental credits (avoided emissions and related impacts) were assigned for any of the other materials sent to recycling. A list of the assumptions on the final fate of all the module components is reported in Table 1.

Regarding the fate of the fraction of spent modules that escape collection ('reference' and 'worst case' scenarios), it is to be noted that the chemical form in which Cd is present in the modules (CdTe) reduces the risk of Cd contamination, even in the event that module scrap ends up in municipal landfills. In particular, broken module scrap has been shown to pass the US EPA Toxicity Characteristic Leaching Procedure (TCLP) test, i.e. Cd concentration in extraction fluid <1 mg/L (Fthenakis 2003). The TCLP test (US EPA 1992) is specifically designed to simulate leaching in a municipal landfill (Kimmel 1999); the regulatory level for any given metal (e.g. Cd) represents a back-calculation from an acceptable chronic exposure level at exposure point (B), to the level at the landfill (A), accounting for dilution and attenuation that is predicted to occur from (A) to (B), according to the EPACML groundwater transport model (US EPA 1990). Cd emissions to water from landfilled CdTe PV module scraps were

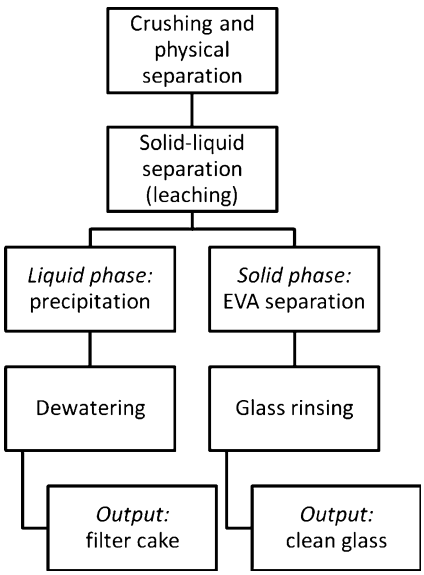

Fig. 1 Flow chart of the CdTe PV module recycling process

Table 1 Assumptions on CdTe PV end-of-life module

Compartment	Sub-compartment	Fate
Cd-containing photoactive layer		Recycling
Encapsulation	Glass	Recycling
	Ethylene vinyl acetate (EVA)	Incineration
	Plastics	Landfill
	Copper	Recycling
Cord plate	Polycarbonate	Landfill
	Solder paste	Landfill
Lead wire	Sn-plated Cu wire	Recycling
	Rubber insulation	Landfill

therefore calculated based on the Cd content in PV modules and the TCLP protocol:

$$\begin{aligned}&\text{TCLP protocol limit}: [1\text{mg(Cd emitted)/L(extraction fluid)}]\\&\quad /[20\text{L(extraction fluid)/kg(waste)}] = 0.05\text{mg(Cd)/kg(waste)}\\&\text{Cd content in PV module waste}: [9.7\text{g(Cd)/m}^2\text{(PVmodule)}]\\&\quad /[16.9\text{kg/m}^2] = 0.57\text{g(Cd)/kg(PVmodule)}\\&\Rightarrow \text{Cd emissions to water from landfilled PV module waste}:\\&\quad [0.05\text{mg(Cd)/kg(waste)}]/[0.57\text{g(Cd)/kg(PV module)}] =\\&\quad = 0.09\text{g(Cd)emitted}\,\textit{per kg of Cd content in PV module scrap.}\end{aligned}$$

Cd emissions to air from CdTe PV module scrap cut to small pieces and exposed to high-temperature fires were experimentally evaluated to be 5 g/kg of Cd content (Fthenakis et al. 2005), which, incidentally, is virtually the same as the amount of Cd emitted the incineration of NiCd batteries (Rydh and Karlström 2002). The remaining Cd in the incinerated PV module scraps ends up encapsulated in the molten glass and therefore causes no further contamination.

For the sake of completeness, the analysis was also extended to include the balance of system (BOS) components, even though the latter's contribution in terms of Cd emissions was expected, and later confirmed to be minor. Use was made of the inventory data produced by an independent study of a modern large-scale PV power plant (Mason et al. 2006). The allocation of the inverter per square metre of PV system was performed on the basis of the nominal 109 Wp/m^2 of the current top performance CdTe PV modules, assuming a lifetime of 30 years for both the PV module and the inverters, with 10% part replacement every 10 years for the latter (Alsema et al. 2009). It was assumed that, at the end of the plant lifetime, the concrete parts (foundations and pillars) would either be left on site for re-use or just abandoned. Most of the valuable steel and aluminium parts were instead assumed to be bought and fetched by the recycling companies, and the environmental burdens associated to their transportation and processing were excluded from the analysis, being virtually allocated to the downstream product systems which make use of the recycled metals (Guinée 2001). In accordance with the European research project ECLIPSE (2004), iron, steel and aluminium were assumed to be 80% recycled and 20% landfilled, and the same assumption was also extended to copper; the remaining BOS materials (epoxy resin and tin) were assumed to be 100% landfilled. All Cd emissions from landfills (other than those from PV module scrap, as explained above) were estimated using the Ecoinvent model, which covers a time span of 60,000 years (Doka 2007).

3 Results and discussion

Because of the large range of uncertainty that is entailed in the computation of life cycle impact assessment characterization factors (equivalent toxicity potentials) when heavy metal emissions are concerned (Heijungs 2004), the choice was made to discuss and compare the results of our analysis at the inventory level, i.e. directly in terms of the amounts of Cd emitted to air and water. Table 2 lists the main contributions to the total Cd emissions to air and water associated to the end-of-life of a CdTe PV system, assuming 100% recycling of the PV modules. As can be seen, direct Cd emissions from the module recycling process are dominant in the case of emissions to water, while the Cd emissions to air are mostly caused by the background processes for the supply of chemical reagents and electricity. The contribution of the end-of-life treatment of the BOS is absolutely negligible.

Table 3 then lists the total Cd emissions to air and water associated to the recycling, incineration and landfilling of CdTe PV, expressed per kilogram of Cd content

Table 2 Main contributions to the end-of-life Cd emissions of a CdTe PV system, assuming 100% recycling of modules

Direct emissions to air (module recycling)	–
Indirect emissions to air	
H_2O_2 for module recycling	55%
Electricity for module recycling	31.4%
NaOH for module recycling	8.5%
H_2SO_4 for module recycling	3.5%
BOS end-of-life	< 0.14%
Direct Cd emissions to water (module recycling)	93%
Indirect emissions to water	
EVA incineration	2.3%
Electricity for module recycling	2%
H_2O_2 for module recycling	1.8%
BOS end-of-life	<0.02%

in the product. It should however be noted that increasing air emission controls in municipal solid waste incineration to treat heavy metal emissions in flue gas are likely to lead to reductions in airborne emissions in the foreseeable future.

Figure 2 shows the resulting Cd emissions to air and water from the end-of-life of CdTe PV, according to the three scenarios described in Section 2. Non-recycled PV modules in the 'worst case' scenario are assumed to be 33% incinerated and 67% landfilled, consistently with the current practice for MSW treatment in the EU-27 (Blumenthal 2011).

Cd emissions to water remain low at ~40 mg of Cd per kg of Cd content, regardless of the considered scenario, due to the extremely low leachability of CdTe. Cd emissions to air are mainly caused by incineration and consequently only become non-negligible (~250 mg of Cd per kg of Cd content) in the 'worst case' scenario, where 5% of the modules end up being disposed of this way.

To put these numbers into perspective, it is worth comparing them to the routine Cd emissions caused by the end-of-life treatment of NiCd rechargeable batteries, which are currently by far the largest consumers of raw cadmium in the world, absorbing about 80% of the primary Cd supply (International Cadmium Association 2011; UNEP 2006). In particular, the average price of portable (sealed) NiCd batteries is two to ten times greater than for the same capacity of industrial NiCd batteries, which makes the market for portable batteries more profitable, and in fact, portables have accounted for approximately two thirds of the total NiCd battery market for the last two decades (David 1995; Pillot 2009). However, portable NiCd batteries are particularly susceptible to being disposed of incorrectly: firstly, there is usually a considerable time lapse between the end of a battery service life and its subsequent contribution to Cd emissions through waste treatment, which is mainly caused by the documented common habit of stockpiling and hoarding spent batteries in the home, as well as in many types of businesses (Vangheluwe et al. 2005). Secondly, in many cases, the fractions of spent batteries entering the different disposal routes are not well known at all, since sealed NiCds may be contained within finished products, and/or assembled in packs containing

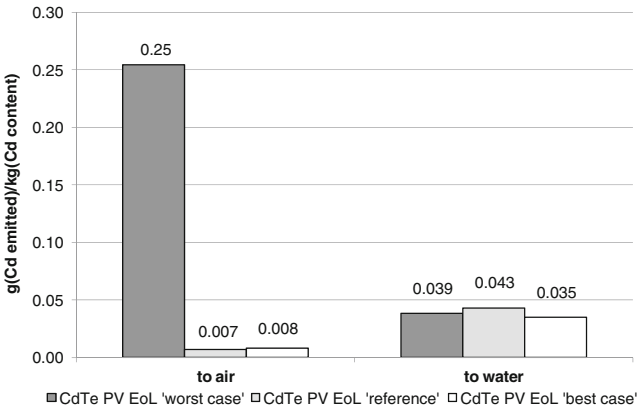

Fig. 2 Cd emissions to air and water from end-of-life of CdTe PV, expressed per kilogram of Cd content ('*best case*'=100% recycling; '*reference*'=85% recycling/15% landfill; '*worst case*'=85% recycling/10% landfill/5% incineration)

variable numbers of cells. Lastly, the typically small size of most portable batteries makes them intrinsically more prone to escape collection and/or selection and recovery. Overall, approximately 80% of portable NiCd batteries escape recycling (David 1995; RECHARGE 2008) and end up dispersed in undifferentiated MSW streams. Thus, recalculating the end-of-life Cd emissions from NiCd batteries reported by Rydh and Karlström (2002), by taking into account that 20% thereof are recycled, (80%·67%)=54% are landfilled and (80%·33%)=26% are incinerated, leads to approximately 1 g of Cd emissions to air and 250 mg of Cd emissions to water, per kilogram of Cd content. Such emission levels are clearly much larger than those found for the end-of-life of CdTe PV, which facilitates a much more stringent control over its end-of-life treatment, and benefits from clear pro-active take-back policies which are already under way. Incidentally, it is also to be noted that NiCd batteries cause additional Cd emissions during their use phase, due to the electricity required to recharge them multiple times; conversely, the Cd emission balance of the CdTe PV system use phase is actually negative, since emissions due to accidental releases are negligible, if any, while PV electricity typically displaces a conventional mix of technologies which cause much higher Cd emissions per kilowatt hour (Fthenakis et al. 2008).

Table 3 End-of-life Cd emissions for recycling, incineration and landfilling of CdTe PV, expressed as grams (Cd)/kilogram (Cd)

	Recycling	Incineration	Landfilling
Cd emissions to air			
CdTe PV	0.008	5	–
Cd emissions to water			
CdTe PV	0.035	–	0.09

4 Conclusions

Results from this study have shown that the actual levels of Cd emissions to air and water from the end-of-life of CdTe PV are relatively low and considerably lower, for instance, than those from the end-of-life of common NiCd batteries. A large-scale deployment of CdTe PV is thus unlikely to result in a significant increase of the overall Cd emissions to the environment, mainly thanks to the stringent control

of Cd-containing PV waste flows, as well as the intrinsically lower leachability and toxicity of CdTe than other Cd compounds.

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